

Coal Gel Chemistry I. An Aspect of Synergistic Effects
on the solvent Swelling of Coal

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INTRODUCTION

For a long time, the mixed solvents, such as alcohol-benzene, are conveniently used for coal extractions(1), in which solubilities of coal products used to be enhanced to those in the individual solvents. Most recently, Iino et al. (2) reported powerful binary solvent systems for coal extractions which were composed of carbondisulfide and aprotic dipolar solvents like a DNF or N-methylpyrrolidinone. Although it has long been pointed out that there was a correlation between the increase of extractability and the increase of swelling(2, 3), the mechanism of the synergistic effect on the solvent swelling of coal has been controversial in the coal chemistry. For examples, the effects observed in the binary solvent systems composed of the amine as a counter component had been discussed by Hombach(4) and Larsen(5), based on the solubility parameters and hydrogen bondings in the coal matrix, respectively.

Meanwhile, recently, we revealed the significant steric requirement on the solvent swelling of coal(6). In the course of the further study on the solvent swelling by using various solvents we have learned that there was a curious similarity on the solvent systems adopted by previous researchers(4,5), which were commonly composed of a sterically hindered and a less sterically hindered solvents, and also have found that the relaxation of the steric requirement of coal by the initial formation of the "Coal Gel" of a less hindered solvent would be responsible to the synergistic effect on the solvent swelling of coal.

This paper presents the results of the studies on the synergistic effects of binary solvents on the solvent swelling of coal, based on the steric requirement.

EXPERIMENTAL

The swelling measurements were carried out as described into previous paper (7). Coal, Illinois #6 coal, used in these studies were from the Ames Laboratory Coal Laibrary. Prior to use, the coal was ground, sized, dried at 110 °C overnight under vacuum, and stored under a nitrogen atmosphere. The solvents were distilled by ordinary procedures before use. The quantitative determination of the ratio of the concentrations of solvents in the system were carried out by a gaschromatography using a packed column($\Phi=1/8'$, glass columnn, 2m, PDEGS). A typical run was as follows: To Illinois #6 coal(500mg; 60-100mesh), a mixture of triethylamine and methanol(1.5ml; 1:2 vol.) was added, and immersed in the ultrasonic cleaning bath. An aliquot of the supernatant of the mixture was injected into a gaschromatography with appropriate time intervals.

RESULTS AND DISCUSSION

Swelling of Illinois #6 Coal in Binary Solvent System

Figure 1. shows the swelling behavior of Illinois #6 coal in the systems of triethylamine and methanol, and dimethylaniline and methanol.

As Hombach already reported(4), in these case also significant synergistic effects were observed. However, curiously enough such effects did not appeared in the systems such as pyridine/methanol or n-propylamine/methanol, in spite of their reasonable ranges of the solubility parameters ,as shown in Figure 2.

Furthermore, in the case of the use of steric isomers of butylamine, n-butylamine and t-butylamine, the synergistic effect was observed only to the sterically hindered isomer system(Figure 3).

Figure 4. shows the solvent swelling behaviors of Illinois #6 coal in the binary solvent systems of which components' solbility parameters are considered to be quite similar, i.e., hexamethylphosphoramide(HMPA) / dimethylformainde (DMF) or t-butylmethylketone(pinacolone) / acetone, in which also sinergistic effects appeared.

These observations clearly suggest that the sinergistic effects of binary solvents on the swelling of coal were not resulted by such simple parameter as a solbility parameter.

Recently, we have revealed the steric requirement on the solvent swelling of coal(6). Based on our observations, such solvents as triethylamine, dimethyl aniline, t-butylamine, pinacolone or HMPA showed significant retardations on

their penetration rates into coal matrix(8). On this point of view, it is quite likely that because of their steric bulkiness, the apparent equilibrium swelling ratios(Q-values) of these solvents are forced to keep far below their potential values expected under more relaxed steric requirement of coal. .

Measuring the Relative Concentrations of Binary Solvents During Swelling of Illinois #6 Coal

In order to examine the possibility of the selective penetration of the solvent molecule of the binary system into the coal matrix, the relative concentrations of the solvents in the supernatant of the mixture were determined during swelling the coal.

Figure 5. illustrated the change of the relative concentration of methanol vs. time, together with the swelling behavior of coal.

It is obvious that the penetration of methanol into the coal matrix occurred predominantly, that is, the relative concentration of methanol in the supernatant was sharply decreased at the initial stage of swelling of coal, and then kept almost constant value which was still a little below the original concentration.

Table 1. shows the relative swelling rate (retardation factors; V_{rel}) of the various solvents to Illinois #6 coal at 21°C, which were calculated as described into previous report(7). In these data, we can see that the penetration rate of methanol is approximately 10⁴ times faster than that of triethylamine.

Plausible Mechanism of Synergistic Effect of Binary Solvent on Swelling of Coal.

All of these observations described above may be rationalized as follows: The swelling of coal in the binary solvent systems composed of a sterically hindered and a less sterically hindered solvents(or in general, the solvents possessing different penetration rates) is initiated by the predominant penetration of the less hindered solvent, and then forms , so-called, "Coal Gel", of which steric requirement will be released significantly because of the expansion of the coal matrix by the penetrant, and thus it enable to penetrate more sterically hindered solvent molecule into coal with a "Edge Effect".

Namely, the synergistic effect of binary solvent on the swelling of coal is considered to be resulted by the relaxation of the steric requirement of coal, based on the "Coal Gel" formation.

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Table 1. Comparison of Swelling Rate
(Illinois #6, 60-100 mesh, 21 °C)

SOLVENTS	$V_{Ret.}^*$
Methanol	1.00
Acetone	0.86
Dimethylformamide	0.24
n-Butylamine	0.10
t-Butylamine	39.75
Dimethylaniline	105.43
Triethylamine	$> 10^4$
Pinacolone	$> 10^3$
Hexamethylphosphoramine	$> 10^4$

* Retardation Factor = $V_{MeOH} / V_{Solvent}$

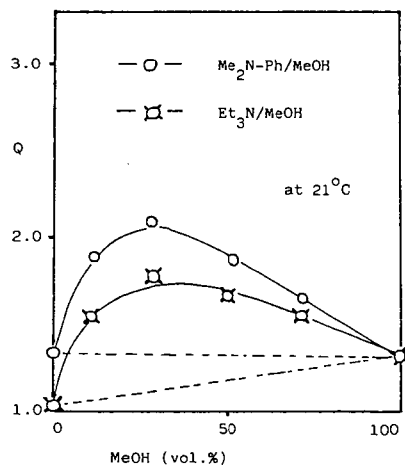


FIGURE 1.

Solvent Swelling of Coal in Binary System
(Illinois #6 Coal, 60/100 mesh)

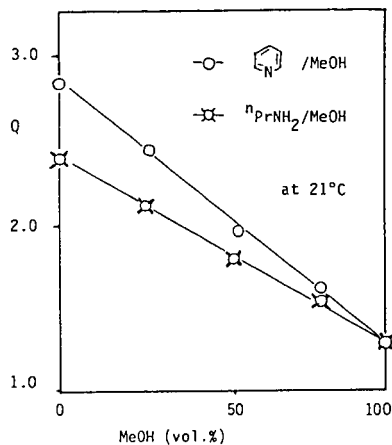


FIGURE 2.

Solvent Swelling of Coal in Binary System
(Illinois #6 Coal, 60/100 mesh)

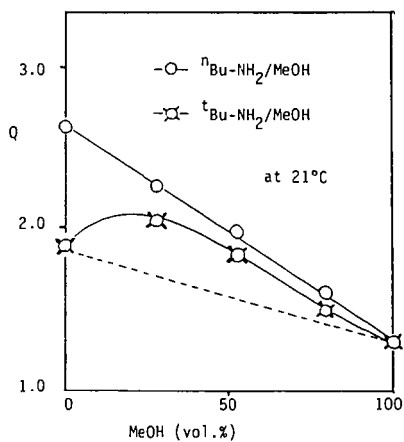


FIGURE 3.

Solvent Swelling of Coal in Binary System
(Illinois #6 Coal, 60/100 mesh)

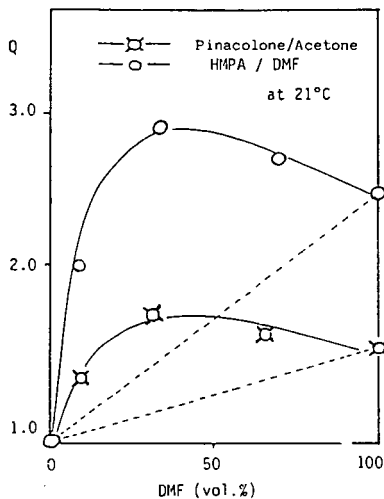


FIGURE 4.

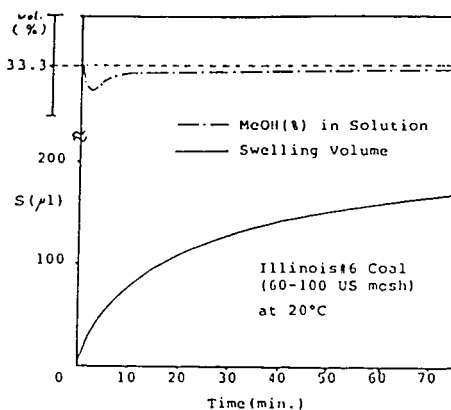


FIGURE 5 Solvent Swelling in Binary Solvent System
(Et₃N/MeOH) and Change of Composition
in Solution